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## **PATENT APPLICATION**

### **CORROSION RESISTANT COATING FOR SEMICONDUCTOR PROCESSING CHAMBER**

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## CORROSION RESISTANT COATING FOR SEMICONDUCTOR PROCESSING CHAMBER

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### BACKGROUND OF THE INVENTION

The present invention relates to equipment used in the manufacture of semiconductor devices. More specifically, the present invention relates to formation of a plasma-resistant coating on the surfaces of selected components of semiconductor manufacturing equipment.

With the development of high density plasma sources and 300 mm-wafer-size reactors, and the growing importance of certain high temperature processing steps, wear on chamber materials may impact tool performance and productivity. Specifically, interaction between corrosive plasmas and reactor materials become of critical importance to development of future product lines of semiconductor manufacturing equipment. Very harsh environments (e.g.,  $\text{NF}_3$ ,  $\text{C}_2\text{F}_6$ ,  $\text{C}_3\text{F}_8$ ,  $\text{ClF}_3$ ,  $\text{CF}_4$ ,  $\text{SiH}_4$ ,  $\text{TEOS}$ ,  $\text{WF}_6$ ,  $\text{NH}_3$ ,  $\text{HBr}$ , etc.) can be found in plasma etchers and plasma-enhanced deposition reactors. Constituents from many of these environments may react with and corrode parent anodized materials such as aluminum oxide.

Because of their favorable physical characteristics, ceramic materials are commonly used in today's semiconductor manufacturing equipment to meet the high process performance standards demanded by integrated circuit manufacturers. Specifically, ceramic materials exhibit high resistance to corrosion, which helps to increase process kit lifetimes and lowers the cost of consumables as compared to other materials such as aluminum or quartz. Example of components that can be advantageously manufactured from ceramic materials include chamber domes for inductively coupled reactors, edge rings used to mask the edge of a substrate support in certain processing chambers, and chamber liners that protect walls of the chamber from direct exposure to plasma formed within the chamber and improve plasma confinement by reducing coupling of a plasma with conductive chamber walls. In some instances, the chamber walls themselves may also be manufactured from ceramic materials.

Ceramic materials are also used for critical components such as high temperature heaters and electrostatic chucks.

Ideally, critical and/or high value ceramic parts of a semiconductor processing tool employed in production should have a lifetime of at least one year.

5 Depending on the particular tool, this can correspond to processing of 50,000 wafers or more without changing any parts on the tool (i.e., a zero consumable situation), while at the same time maintaining high process performance standards. For example, to meet the requirements of some manufacturers, less than 20 particles of size of greater than 0.2  $\mu\text{m}$  should be added to the wafer during the processing of the wafer in the chamber.

10 However, unwanted particle generation is an issue for high temperature applications where processing temperatures exceed 550°C. For example, in highly corrosive fluorine and chlorine environments,  $\text{Al}_2\text{O}_3$  and  $\text{AlN}$  ceramic materials may corrode to form unwanted  $\text{AlO:F}$ ,  $\text{AlF}_x$ , or  $\text{AlCl}_x$  films at the component surface. These  $\text{AlO:F}$ ,  $\text{AlF}_x$ , or  $\text{AlCl}_x$  films have relatively high vapor pressures and relatively low  
15 sublimation temperatures. For example, the sublimation temperature of aluminum chloride ( $\text{AlCl}_x$ ) is approximately 350°C and the sublimation temperature of aluminum fluoride ( $\text{AlF}_x$ ) is approximately 600°C. If a ceramic component is employed at a temperature exceeding the sublimation temperature, the outer surface of the component may be consumed by the process of formation of  $\text{AlO:F}$ ,  $\text{AlF}_x$  or  $\text{AlCl}_x$ . This  
20 consumption of material can degrade the chamber component and/or introduce particles into the process.

In light of the above, improvement in the corrosion resistance of various substrate processing chamber parts and components is desirable.

## SUMMARY OF THE INVENTION

25 The present invention provides a method for improving the corrosion resistance of components of semiconductor tools by creating high temperature halogen corrosion resistant surface coatings. Specifically, coatings of rare earth-containing materials are formed over the surfaces of ceramic tool components. These rare earth-containing materials are stable in plasma environments at high temperatures and may  
30 be formed onto the chamber components by sputter deposition. To promote adhesion of the coating to the parent material, an adhesion layer may be first formed on the

ceramic material by accelerating rare earth ions into the surface of the ceramic material at changed energies to form an implant layer prior to formation of the surface coating.

An embodiment of a substrate processing chamber in accordance with the present invention includes at least one component bearing a rare earth-containing coating bound to a parent material by an intervening adhesion layer, such that the component exhibits resistance to etching in a plasma environment.

An embodiment of a method for treating a parent material for resistance to plasma etching comprises forming an adhesion layer over a parent material, and forming a rare earth-containing coating over the adhesion layer.

These and other embodiments of the present invention, as well as its advantages and features, are described in more detail in conjunction with the text below and attached figures.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1A is a simplified cross-sectional view of a high density plasma chemical vapor deposition chamber;

Fig. 1B is a simplified cross-sectional view of a capacitively coupled plasma enhanced chemical vapor deposition chamber;

Fig. 2A is a cross-sectional view of a coated member in accordance with a first embodiment of the present invention;

Fig. 2B is a cross-sectional view of a coated member in accordance with a second embodiment of the present invention;

Fig. 3 is a simplified schematic view of a Metal Plasma Immersion Ion Implantation and Deposition (MEPIID) technique;

Fig. 4 is a graph illustrating the concentration of rare earth ions at various depths in a ceramic component treated with MEPIID;

Fig. 5 is a simplified cross-sectional view of an exemplary metal vapor vacuum arc implanter used in the MEPIID technique;

Fig. 6 is a simplified schematic view of an Ion Bombardment Assisted Deposition (IBAD) technique;

Fig. 7A shows a magnified (2000X) view of the top surface of a first grade of an AlN coupon following exposure to a fluorine ambient at high temperature.

Fig. 7B shows a further magnified (7500X) view of the top surface of the AlN coupon of Fig. 7A.

Fig. 7C shows a magnified (2000X) view of the top surface of a second grade of an AlN coupon following exposure to a fluorine ambient at high temperature.

Fig. 7D shows a further magnified (7500X) view of the top surface of the AlN coupon of Fig. 7C.

Fig. 8A shows a magnified (2000X) view of the top surface of a first grade of an AlN coupon coated with yttrium oxide by reactive sputtering in accordance with an alternative embodiment of the present invention.

Fig. 8B shows a further magnified (7500X) view of the top surface of the AlN coupon of Fig. 8A.

Fig. 8C shows a magnified (2000X) view of the top surface of the AlN coupon of Figs. 8A-B following exposure to a fluorine ambient at high temperature.

Fig. 8D shows a magnified (7500X) view of the top surface of the AlN coupon of Fig. 8C.

Fig. 8E shows a magnified (2000X) view of the top surface of a second grade of an AlN coupon coated with yttrium oxide by reactive sputtering in accordance with an alternative embodiment of the present invention.

Fig. 8F shows a further magnified (7500X) view of the top surface of the coated AlN coupon of Fig. 8E.

Fig. 8G shows a magnified (2000X) view of the top surface of an AlN coupon coated with in accordance with one embodiment of the present invention, following exposure to a fluorine ambient at high temperature.

Fig. 8H shows a further magnified (7500X) view of the top surface of the AlN coupon of Fig. 8G.

Fig. 9A shows a magnified (2000X) view of the top surface of an AlN coupon implanted with yttrium in accordance with one embodiment of the present invention.

Fig. 9B shows a further magnified (7500X) view of the top surface of the implanted AlN coupon of Fig. 9A.

Fig. 9C shows a further magnified (9000X) view of the fractured AlN coupon of Figs. 9A-9B.

Fig. 9D shows a magnified (2000X) view of the surface of the implanted AlN coupon of Figs. 9A-9C following exposure to a fluorine ambient at high temperature.

5 Fig. 9E shows a further magnified (7500X) view of the surface of the implanted AlN coupon of Fig. 9D.

Fig. 10A shows a magnified (3300X) view of a fractured AlN coupon implanted with yttrium oxide following exposure to a fluorine ambient at high temperature.

10 Fig. 10B shows a further magnified (7500X) view of the fractured AlN coupon of Fig. 10A.

Fig. 11 shows the results of Energy Dispersive Spectroscopy (EDS) of the surface of the AlN coupon of Figs. 10A-10B coated in accordance with an embodiment of the present invention, following exposure to a fluorine ambient at high temperature.

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## DESCRIPTION OF THE SPECIFIC EMBODIMENTS

According to the present invention, ceramic components of semiconductor fabrication tools, including but not limited to electrostatic chucks, gas nozzles, chamber domes, heated pedestals, gas distribution manifolds, chamber walls and chamber liners, may be coated with a rare earth-containing material and adhesion layer in order to improve corrosion resistance. Environments for which the coated components can be advantageously used include, but are not limited to, highly corrosive plasma etching environments, and high temperature deposition environments that feature corrosive gases.

### 25 I. Exemplary Substrate Processing Chambers

Figs. 1A and 1B are simplified cross-sectional views of exemplary substrate processing chambers in which ceramic components made according to the method of the present invention may be employed. Fig. 1A is a simplified cross-sectional view of a high density plasma chemical vapor deposition (HDP-CVD) chamber 10 such as an Ultima HDP-CVD substrate processing chamber manufactured by Applied Materials, the assignee of the present invention. In Fig. 1A, substrate processing chamber 10 includes a vacuum chamber 12 in which a substrate

support/heater 14 is housed. Substrate support/heater 14 includes an electrostatic chuck 15 that securely clamps substrate 16 to substrate support/heater 14 during substrate processing.

When substrate support/heater 14 is in a processing position (indicated by dotted line 18), deposition and carrier gases are flowed into chamber 10 via gas injection nozzles 20. Nozzles 20 receive gases through gas supply lines, which are not shown. Chamber 10 can be cleaned by the introduction of fluorine radicals or other etchant radicals that are dissociated in a remote microwave plasma chamber (not shown) and delivered to chamber 10 through a gas feed port 22. Unreacted gases and reaction byproducts are exhausted from the chamber 10 by a pump 24 through an exhaust port on the bottom of the chamber. Pump 24 can be isolated from chamber 10 by a gate valve 26.

The rate at which deposition, carrier and clean gases are supplied to chamber 10 is controlled by a mass flow controllers and valves (not shown), which are in turn controlled by computer processor (not shown). Similarly, the rate at which gases are exhausted from the chamber is controlled by a throttle valve 28 and gate valve 26, which are also controlled by the computer processor.

A plasma can be formed from gases introduced into chamber 10 by application of RF energy to independently controlled top coil 30 and side coil 32. Coils 30 and 32 are mounted on a chamber dome 34, which defines the upper boundary of vacuum chamber 12. The lower boundary of vacuum chamber 12 is defined by chamber walls 36. Substrates can be loaded into chamber 10 and onto chuck 15 through an opening 38 in chamber wall 36.

According to the present invention, any or all of electrostatic chuck 15, gas nozzles 20, and chamber dome 34 of substrate support/heater 14 may be fabricated from material implanted with rare-earth ions.

Fig. 1B is a simplified cross-sectional view of a capacitively-coupled plasma enhanced chemical vapor deposition chamber (PECVD) 50 such as the CxZ CVD substrate processing chamber manufactured by Applied Materials, the assignee of the present invention. In Fig. 1B, substrate processing chamber 50 includes a vacuum chamber 52 in which a heated pedestal 54 and a gas distribution manifold 56 are housed. During processing, a substrate 58 (e.g., a semiconductor wafer) is positioned on a flat or slightly convex surface 54A of pedestal 54. The pedestal can be

controllably moved between a substrate loading position (depicted in Fig. 1B) and a substrate processing position (indicated by dashed line 60 in Fig. 1B), which is closely adjacent to manifold 56.

Deposition, carrier and cleaning gases are introduced into chamber 52 through perforated holes 56A of a gas distribution faceplate portion of manifold 56. More specifically, gases input from external gas sources (not shown) flow into the chamber through the inlet 62 of manifold 56, through a conventional perforated blocker plate 64 and then through holes 56A of the gas distribution faceplate. Gases are exhausted from chamber 52 through an annular, slot-shaped orifice 70 surrounding the reaction region and then into an annulate exhaust plenum 72. Exhaust plenum 72 and slot-shaped orifice 70 are defined by ceramic chamber liners 74 and 76 and by the bottom of chamber lid 57.

The rate at which deposition, carrier and clean gases are supplied to chamber 50 is controlled by mass flow controllers and valves (not shown), which are in turn controlled by computer processor (not shown). Similarly, the rate at which gases are exhausted from the chamber is controlled by a throttle valve (not shown and also controlled by the computer processor) connected to exhaust port 66, which is fluidly-coupled to exhaust plenum 72.

The deposition process in chamber 50 can be either a thermal or a plasma-enhanced process. In a plasma-enhanced process, an RF power supply (not shown) provides electrical energy between the gas distribution faceplate and an electrode 68A within pedestal 54 so as to excite the process gas mixture to form a plasma within the generally cylindrical region between the faceplate and pedestal. This is in contrast to an inductive coupling of RF power into the gas, as is provided in the chamber configuration shown in Figure 1A. In either a thermal or a plasma process, substrate 58 can be heated by a heating element 68B within pedestal 54.

According to the present invention, any or all of pedestal 54, heating element 68B gas distribution manifold 56, and chamber liners 74 and 76 may be constructed from a ceramic material implanted with rare-earth ions according to the present invention. The embodiments of Figs. 1A and 1B are for exemplary purposes only, however. A person of skill in the art will recognize that other types of ceramic parts in these and other types of substrate processing chambers in which highly corrosive environments are contained (e.g., reactive ion etchers, electron cyclotron



resonance plasma chambers, etc.) may benefit from the teaching of the present invention.

## II. Coating Formation

In accordance with embodiments of the present invention, parent materials of components of semiconductor fabrication apparatuses are protected against corrosion by a surface coating containing a rare earth metal, the coating exhibiting low reactivity to a halogen gas environment at elevated temperatures. For purposes of this patent application, yttrium is considered a rare earth metal.

Surface coatings in accordance with embodiments of the present invention maintain adhesion to the parent material at high operating temperatures (up to 1000°C). The surface coatings may include yttrium fluoride, yttrium oxides, yttrium-containing oxides of Aluminum ( $YAlO_3$ ,  $Y_3Al_5O_{12}$ ,  $Y_4Al_2O_9$ ), Erbium oxides, Neodymium oxide, and other rare earth oxides.

The high operating temperatures of many plasma processes can create problems arising from a lack of adhesion between a parent material and an overlying coating. Accordingly, it is useful to form an adhesion layer between the coating and parent material.

This is illustrated in Fig. 2A, which is a cross-sectional view of coated member 215 in accordance with an embodiment of the present invention. As shown in Fig. 2A, adhesion layer 212 overlies parent material 214, and coating 216 is formed over adhesion layer 212. Parent material 214 may comprise AlN,  $Al_2O_3$ , or some other material. In accordance with one embodiment of the present invention, rare earth-containing coating 216 may be deposited over adhesion layer 212 by sputtering techniques. Sputtering may take place in a particular ambient, for example by reactive sputtering of a target of the rare earth material in an oxygen ambient to create a rare earth oxide coating.

Adhesion layer 212 may exhibit a coefficient of thermal expansion intermediate that of parent material 214 and coating 216, such that coating 216 adheres to parent material 214 over a wide temperature range. The adhesion layer may be formed over the substrate by deposition prior to formation of the coating.

In alternative embodiments in accordance with the present invention, the adhesion layer may be formed by accelerating rare earth ions toward the parent material

at changed energies prior to formation of the surface coating. For example, adhesion layer 212 of structure 215 of Fig. 2A may result from ion-implantation, with reduction over time in the energy of implantation of rare earth metals into parent material 214 creating implanted adhesion layer 212. Implanted adhesion layer 212 may be graded,  
5 with the rare earth metal concentration gradient determined by duration of implantation at particular energy levels.

Acceleration of rare-earth ions to a depth into the target parent material may be accomplished using a variety of techniques. In one implantation approach, rare earth ions are introduced into the parent material utilizing metal plasma ion immersion  
10 implantation and deposition (MEPIIID). Fig. 3 shows a simplified schematic view of the MEPIIID technique.

As shown in Fig. 3, single or dual-source MEPIIID source 300 is used to implant and deposit a layer of rare-earth ions over the component 300 being treated. With this technique, component 302 is inserted into plasma 304 after plasma 304 has  
15 been deflected with magnetic filter 304. Sheath edge 311 represents a concentrated plasma zone near biased target component 302, where most reactions and rearrangements of materials occur.

The treated component 302 is then subjected to implantation by biasing component 302 with a negative voltage utilizing electrode 307 in communication with  
20 power supply 306. When target component 302 is unbiased, it is subject to the initial deposition phase of the treatment process. When target component 302 is negatively biased (e.g., at - 50 keV), ions 310 from plasma 304 are accelerated toward target component 302 at high velocities so that target component 302 is subjected to ion implantation to a depth into the material. The magnitude of the negative bias of the  
25 target material, and hence the energy of bombardment, is then reduced to produce a gradient of concentration of rare earth material to a depth in the material.

A more detailed description of a single-source MEPIIID system is set forth in U.S. Patent 5,476,691 issued to Ian Brown et al., hereby incorporated by reference in its entirety. In a technique employing a dual-source MEPIIID implanter,  
30 the treatment process is similar except that plasmas from two separate plasma guns are brought together through independent magnetic channels, in order to deposit a thin film over the parent component.

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The MEPIIID approach to implantation of rare earth metals requires that the component be subject to an electrical bias. However, such biasing is not possible with parent materials that are poor conductors. This issue can be resolved if an electrode is embedded within the component, the embedded electrode capable of being biased during the implantation step. Such is the case for heaters and electrostatic chucks.

Fig. 4 is a graph that shows the concentration of rare-earth ions and aluminum nitride at various depths of an aluminum nitride component treated with a MEPIIID technique. As can be seen in Fig. 4 the upper surface of the treated component comprises a layer M of rare-earth material formed from the deposition phases of the treatment process. Beneath layer M, the concentration of rare-earth ions decreases with depth until point N, where the concentration of rare-earth ions reaches background levels (essentially zero).

Because of this profile of implanted material, a graded interface is obtained between the coated surface and the bulk of the parent material. An interface of this type provides a gradual transition of surface properties such as physical and chemical properties, and results in improved adhesion as compared to more abrupt, stepped profile distributions. Such a graded interface also eliminates limitations of adhesion due to thermal mismatch - often a limiting factor of corrosion resistant coatings having an abrupt interface.

In components having an abrupt transition between coating and parent material, the protective coating deposited over chamber materials may crack in response to environmental stresses. For example, during high temperature thermal cycles the temperature change during and/or between various cycles can be as high as 700°C for ceramic heater applications. Another example of an environmental stress that may induce cracking of a coating are the mechanical stresses associated with wafer handling.

Once a crack in a coating is initiated, in a corrosive environment aggressive and corrosive free radicals may penetrate the film coating and erode the underlying wall material. This penetration may cause film delamination and particulate contamination.

By contrast, corrosion-resistant coatings in accordance with  
embodiments of the present invention may serve as a barrier to the diffusion of reactive  
species into the parent material. In this respect, implanted structures may have superior  
performance and versatility as compared with structures formed by plasma spray, CVD,  
5 laser ablation or PVD deposition techniques.

Fig. 5 is a simplified cross-sectional view of an exemplary MEPIIID™  
ion implanter 500 useful to implant ceramic components with rare-earth metals  
according to this embodiment of the present invention. Implanter 500 includes a  
cathode 502 of the desired metal atoms or alloy to be implanted, an anode 504, a  
10 plasma extractor 506, a trigger 508, a cavity 510, and an insulative bushing 512 all  
surrounded by an outer frame 514.

The vacuum arc is a plasma discharge that takes place between  
cathode 502 and the grounded anode 504. The plasma is generated at a number of tiny  
points on the surface of the cathode, called cathode spots and having a dimension of  
15 few microns. The arc is concentrated to an extremely high current density, in the order  
of  $10^8$ - $10^{12}$  A/cm<sup>2</sup>. The metal ions are extracted from the plasma using perforated  
extraction grids 506 which are polarized at appropriate conditions to accelerate the  
extracted ions toward the ceramic component target. Such MEPIIID™ ion sources are  
efficient and do not require a background gas -- the plasma generation process is  
20 neither an evaporative nor a sputtering process. A more detailed description of a  
MEPIIID™ ion implanter similar to the one shown in Fig. 5 is given in U.S. Patent  
5,013,578 issued to Ian Brown et al. The '578 patent is hereby incorporated by  
reference in its entirety.

In the past, MEPIIID™ implanters have typically been used for metal  
25 surface treatment in the automotive industry (e.g., piston surface treatment) and the  
tooling industry for increased hardness. However, one limitation of such commercially  
available implanters is their anisotropy, e.g., the limitation to implant flat surfaces only.  
This is perfectly acceptable to implant the exposed face of flat ceramic heaters or  
electrostatic chucks, but it is a limitation in treating complex-shaped ceramic parts.

30 Manufacturability of a commercially feasible MEPIIID™ implanter  
based on a design similar to that shown in Fig. 5 has been established, however, in  
which large-area or complex-shaped parts could be treated in an industrial scale, high

dose implanter. A description of such implanter is set forth by Ian Brown in Brown, et al., "Metal Ion Implantation for Large Scale Surface Modification," J. Vac. Sci. Tech., A 11(4), July 1993, which is hereby incorporated by reference in its entirety.

While the MEPIIID technique is described above in conjunction with  
5 formation of an adhesion layer for a rare-earth containing coating in accordance with one embodiment of the present invention, the present invention is not limited to use of any particular fabrication technique. For example, an alternative embodiment for forming a corrosion-resistant coating in accordance with embodiments of the present invention utilizes Ion Bombardment Assisted Deposition (IBAD) to accelerate rare  
10 earth metals into the parent material.

Specifically, Fig. 6 shows rare earth metal 601 such as Yttrium sputtered onto the surface of parent material 604 while ion gun 600 accelerates ion beam 602 of inert Argon ions at high (~ 10-12 keV) energies against coated target parent material 604. As a result of the high energy of ion bombardment, deposited metal 601  
15 is driven to a depth within parent material 604. Over time, the energy of the ion beam is then reduced to a lower level (~ 0.5 keV), such that deposited rare earth remains on the surface as a coating rather than being driven into the parent material. In this manner a graded adhesion layer may be formed, with the concentration of rare earth metals in the adhesion layer determined by the duration of bombardment at a particular  
20 reduced energy level.

As a result of deposition of rare earth metal under these conditions, graded subsurface rare earth layer 612 lies between coating 608 and parent material 604, promoting adhesion between coating 608 and parent material 604. Performing such deposition in an oxygen ambient can cause the rare earth metal to react with  
25 oxygen to form rare earth oxide coating 608 over parent material 604.

Having fully described several embodiments in accordance with the present invention, many other equivalent or alternative embodiments of the present invention will be apparent to those skilled in the art. For example, in accordance with an alternative embodiment of the present invention, a coating and/or adhesion layer  
30 may be formed by a chemical vapor deposition (CVD) process rather than a physical vapor deposition process.

Moreover, in accordance with yet another alternative embodiment of the present invention, a plasma resistant coating may take the form of a multi-layer

structure. This is shown in Fig. 2B, which depicts a cross-sectional view of a coated member 219 in accordance with yet another alternative embodiment in accordance with the present invention. In Fig. 2B, coating 220 overlies adhesion layer 222 which in turn overlies parent material 224. Coating 220 itself is comprised of successive layers 220a-220b. Such successive layers may create complementary diffusion barriers, i.e. a yttrium-containing coating layer may serve to inhibit unwanted diffusion of fluorine, while a complementary nitrogen-containing coating layer may serve to inhibit unwanted diffusion of oxygen. Multiple layers of the coating could be formed by successive deposition steps, successive ion implantation steps, or ion implantation in conjunction with deposition.

In certain embodiments, one or both of layers 220a-220b may function as a barrier to inhibit unwanted diffusion of specific chemical species from the chamber environment into the parent material during plasma exposure. For example, a layer of yttrium fluoride could serve to inhibit unwanted diffusion of fluorine through the coating. Similarly, a nitride-containing layer could serve to inhibit unwanted diffusion of oxygen through the coating.

Alternatively, or in conjunction with a barrier diffusion layer, a multilayer coating in accordance with the present invention may include layers having a different thermal modulus, such that thermal conditions possibly inducing unwanted cracking in one layer of the coating will not produce similar cracking in another layer, thereby ensuring the integrity of the coating as a whole.

### III. Experimental Results

In order to illustrate the corrosion resistance imparted by embodiments of the present invention, various samples of coated and uncoated AlN parent materials were subjected to a highly corrosive environment in the form of  $\text{NF}_3$  gas at  $500^\circ\text{C}$  for 200 hours. Two grades of AlN were tested, and the coatings were formed with an approximate thickness of  $1\mu\text{m}$ . A first grade of AlN having a purity of approximately 95% is most commonly used and exhibits high thermal conductivity characteristics favored in heater applications. A second grade of AlN having a purity of approximately 99.9% is less commonly used and exhibits lower thermal conductivity as compared with the first grade of AlN, but has smaller grain size allowing strong

adhesion to overlying coatings. The various experimental conditions are summarized below in TABLE A.

TABLE A

TABLE A

Corrosion Test = 200 hrs. in  $\text{NF}_3$  ambient at  $500^\circ\text{C}$ 

FIG. NO.	Grade of AlN Parent Material	Coating Material	Adhesion Layer (Y)	View	Mag.	Conditions
7A	1 <sup>st</sup>	None	None	Top	2000X	Corrosion Test
7B	1 <sup>st</sup>	None	None	Top	7500X	Corrosion Test
7C	2 <sup>nd</sup>	None	None	Top	2000X	Corrosion Test
7D	2 <sup>nd</sup>	None	None	Top	7500X	Corrosion Test
8A	1 <sup>st</sup>	YO	Sputtering	Top	2000X	Pre- Corrosion Test
8B	1 <sup>st</sup>	YO	Sputtering	Top	7500X	Pre- Corrosion Test
8C	1 <sup>st</sup>	YO	Sputtering	Top	2000X	Corrosion Test
8D	1 <sup>st</sup>	YO	Sputtering	Top	7500X	Corrosion Test
8E	2 <sup>nd</sup>	YO	Sputtering	Top	2000X	Pre- Corrosion Test
8F	2 <sup>nd</sup>	YO	Sputtering	Top	7500X	Pre- Corrosion Test
8G	2 <sup>nd</sup>	YO	Sputtering	Top	2000X	Corrosion Test
8H	2 <sup>nd</sup>	YO	Sputtering	Top	7500X	Corrosion Test
9A	1 <sup>st</sup>	Y	MEPIIID	Top	2000X	Pre- Corrosion Test
9B	1 <sup>st</sup>	Y	MEPIIID	Top	7500X	Pre- Corrosion Test
9C	1 <sup>st</sup>	Y	MEPIIID	Fracture	9000X	Pre- Corrosion Test
9D	1 <sup>st</sup>	Y	MEPIIID	Top	2000X	Corrosion Test
9E	1 <sup>st</sup>	Y	MEPIIID	Top	7500X	Corrosion Test
10A	1 <sup>st</sup>	YO	MEPIIID	Fracture	3300X	Corrosion Test
10B	1 <sup>st</sup>	YO	MEPIIID	Fracture	7500X	Corrosion Test

In a first experiment, uncoated coupons of the two grades of AlN parent material were exposed to the corrosive conditions. Fig. 7A shows a magnified (2000X) view of the top surface of a coupon of the first grade of AlN following exposure to a fluorine ambient at high temperature. Fig. 7B shows a further magnified (7500X) view of the top surface of the AlN coupon of Fig. 7A.

Fig. 7C shows a magnified (2000X) view of the top surface of coupon of the second grade of AlN following exposure to a fluorine ambient at high temperature. Fig. 7D shows a magnified (7500X) view of the top surface of the AlN coupon of Fig. 7C.



As expected, Figs. 7A-7D reveal formation of  $\text{AlF}_3$  crystals on the surfaces of both grades of AlN parent material in the presence of a corrosive fluorine ambient. Formation of this  $\text{AlF}_3$  material reflects corrosion of the parent AlN material.

In a second experiment, a yttrium adhesion layer was formed by sputter deposition over coupons of the first and second grade of AlN, with later portions of the deposition process taking place on an oxygen ambient to create the surface YO coating. Fig. 8A shows a magnified (2000X) view of the top surface of the first grade AlN coupon sputtered with yttrium oxide in accordance with one alternative embodiment of the present invention. Fig. 8B shows a further magnified (7500X) view of the top surface of the AlN coupon of Fig. 8A. Fig. 8C shows a magnified (2000X) view of the top surface of the AlN coupon of Figs. 8A-B following exposure to a fluorine ambient at high temperature. Fig. 8D shows a magnified (7500X) view of the top surface of the AlN coupon of Fig. 8C.

Fig. 8E shows a magnified (2000X) view of the top surface of a second grade AlN coupon coated with yttrium oxide in accordance with the embodiment of the present invention just described. Fig. 8F shows a further magnified (7500X) view of the top surface of the coated AlN coupon of Fig. 8E.

Fig. 8G shows a magnified (2000X) view of the top surface of the AlN coupon of Fig. 8E coated with in accordance with one embodiment of the present invention, following exposure to a fluorine ambient at high temperature. Fig. 8H shows a further magnified (7500X) view of the top surface of the AlN coupon of Fig. 8G.

Figs. 8A - 8H show that the yttrium oxide coating deposited by reactive sputtering converted to dense, even coverage of yttrium fluoride (YF) in the presence of fluorine and high temperatures.

In a third experiment, coupons of the first grade of AlN were ion implanted with yttrium using MEPIIID to form an adhesion layer, and then the energy of implantation was reduced to produce a coating of yttrium on the coupon surface. Fig. 9A shows a magnified (2000X) view of the top surface of an AlN coupon implanted with Y using MEPIIID in accordance with one embodiment of the present invention. Fig. 9B shows a further magnified (7500X) view of the top surface of the implanted AlN coupon of Fig. 9A. Fig. 9C shows a further magnified (9000X) view of the fractured AlN coupon of Figs. 9A-9B.

Fig. 9D shows a magnified (2000X) view of the surface of the AlN coupon of Figs. 9A-9C following exposure to a fluorine ambient at high temperature. Fig. 9E shows a further magnified (7500X) view of the surface of this exposed coupon.

Figs. 9A-9E show that the yttrium coating over the graded adhesion layer resulting from a reduced energy of implantation by MEPIIID was converted by reaction with fluorine to dense, even coverage of yttrium fluoride (YF). Because of its low vapor pressure and high sublimation temperature, this yttrium fluoride coating is expected to be much more stable than  $\text{AlF}_3$ .

In a fourth experiment, the coupons of the first grade of AlN were implanted using MEPIIID to form the adhesion layer, with latter stages of the implant process at reduced implant energies occurring in an oxygen ambient to create a YO surface coating. Figures 10A and 10B show formation utilizing MEPIIID of a yttrium oxide coating on an AlN coupon, followed by exposure to a fluorine ambient at high temperature. Fig. 10A shows a magnified (3300X) view of a fractured coated AlN coupon following exposure to a fluorine ambient at high temperature. Fig. 10B shows a further magnified (7500X) view of the AlN coupon of Fig. 10A.

Figs. 10A-10B show that upon exposure to fluorine plasma, the yttrium oxide coating converted to dense, even coverage of yttrium fluoride (YF). In addition, good adhesion of the YF coating to the parent material was observed. Specifically, upon fracture of the coated coupon as shown in Figs. 10A-10B, the YF coating at the fracture point remained in place, whereas an  $\text{AlF}_3$  coating would be expected to flake off at the fracture point.

The identity of the YF coating on the AlN coupon of Figs. 10A-B subject to MEPIIID implantation is further evidenced by Fig. 11, which shows the results of Electron Dispersive Spectroscopy (EDS) of the surface of the coupon of Figs. 10A-10B. EDS shows the coupon coating to be made up almost entirely of YF.

While the above experimental results illustrate formation of coatings imparting resistance to corrosion to fluorine-based plasmas, the present invention is not limited to this particular application. Resistance to corrosion in other types of plasma environments, including but not limited to chlorine-based plasmas, may also be imparted to chamber components by coatings in accordance with other embodiments of the present invention.

Moreover, while the above description focuses upon the formation of coatings and adhesion layers including yttrium, the present invention is not limited to use of this particular rare earth element. Coatings and adhesion layers in accordance with embodiments of the present invention may be formed utilizing a variety of rare  
5 earth metals, including but not limited to Sc, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu.

Having fully described several embodiments of the present invention, many other equivalent or alternative embodiments of the present invention will be apparent to those skilled in the art. These equivalents and alternatives are intended to  
10 be included within the scope of the present invention and the following claims.